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DOCUMENT-IDENTIFIER: US 6346813 B1

TITLE: Magnetic resonance method for characterizing fluid samples withdrawn from subsurface formations

US Patent No. (1):
6346813Brief Summary Text (6):

In an undisturbed reservoir, formation fluids sometimes partially support the overburden pressure of the earth. When a fluid-bearing formation is penetrated by drilling, formation fluids will flow into the borehole if it is at a lower pressure. The uncontrolled escape of combustible hydrocarbons to the surface ("blowout"), is extremely dangerous, so oil wells are drilled under pressure. During drilling, fluid ("mud") is circulated through the well to carry rock chips to the surface. The mud is densified with heavy minerals such as barite (barium sulfate, 4.5 g/cm^{sup.3}) to ensure that borehole pressure is higher than formation pressure. Consequently, fluid is forced into the formation from the borehole ("invasion"). Usually particles are prevented from entering the formation by the filtering action of the porous rock. Indeed, the filtration process is self-limiting because solids, purposely mixed in the drilling fluid, form a filter cake ("mud cake") at the surface of the borehole. Nonetheless liquid ("mud filtrate") can penetrate quite deeply--as much as several meters into the formation. The filtrate can be either water with various soluble ions, or oil, depending on the type of mud used by the driller. Therefore, the fluid samples withdrawn are mixtures of native formation fluids (including gas, oil and/or water) and the filtrate of mud that was used to drill the well.

Brief Summary Text (15):

Only about six samples can be collected on each descent ("trip") of the tool into the borehole. Because fluid sampling tools are deployed from drilling rigs, and because the rental charge for such rigs can exceed \$150,000 per day in the areas where fluid sampling is most often conducted, economic considerations usually preclude multiple trips in the hole. Thus, oil producing formations are almost always undersampled.

Detailed Description Text (9):

An array of permanent magnets 25 is placed outside the thick-wall metal tube. These create a constant magnetic field, conventionally called B.sub.o, substantially perpendicular to the B.sub.1 field generated by the antenna. To make chemical shift measurements (see below) B.sub.o is preferably substantially uniform in the volume occupied by fluid. However, to measure relaxation time, diffusion coefficient, or spin density of hydrogen or other elements, B.sub.o need not be particularly uniform. One suitable arrangement of permanent magnets is described by Halbach [K. Halbach, Nuc. Inst. Methods 169, 1-10 (1980); K. Halbach, Nuc. Inst. Methods 187, 109-117 (1981)].

Detailed Description Text (17):

All standard NMR measurements can be made using the apparatus described. These include measurements of spin density (proportional to NMR signal amplitude), longitudinal and transverse relaxation times T.sub.1 and T.sub.2 and, more generally, their distributions [R. L. Kleinberg, "Well Logging", Encyclopedia of Nuclear Magnetic Resonance, volume 8 pg 4960-4969, John Wiley & Sons, 1996];

diffusion coefficient and other q-space measurements [P. Callaghan, "Principles of Nuclear Magnetic Resonance Microscopy", Clarendon Press, 1991]; flow velocity measurements [A. Caprihan and E. Fukushima, "Flow Measurements by NMR", Physics Reports, 198, 195-235 (1990)]; and chemical shift spectroscopy when the B.sub.o field is sufficiently uniform [H. J. Vinegar "Method of Determining Preselected Properties of a Crude Oil", U.S. Pat. No. 5,306,640 (1994)].

Detailed Description Text (28):

Many wells are drilled with muds in which oil is the continuous phase. These muds are comprised of hydrocarbons ("base oil"), typically hexadecanes, plus salt water, solids, and chemical additives. Usually only the base oil, together with oil-soluble additives, enter the formation and mix with formation oils. Water and solids remain in the borehole, or form a filter cake on the borehole wall. The oil entering the formation is called "oil base mud filtrate".

Detailed Description Text (29):

There are a number of NMR-detectable contrasts between oil base mud (OBM) filtrates and formation oils: (1) viscosity, (2) composition, (3) trace element content (natural or introduced), (4) diffusion coefficient, (5) proton density, and (6) molecular conformation.

Detailed Description Text (37):

NMR-active nuclei can be monitored directly to determine contamination levels. OBM filtrates may differ from native oils by having substantially different concentrations of oxygen, sulfur, or nitrogen. Of these, nitrogen is the best NMR target because its NMR-active form, ¹⁴N, has good NMR sensitivity and a reasonable natural abundance, see Table hereinbelow. Considerably greater sensitivity to contamination can be attained if trace elements are mixed with the drilling mud to mark the filtrate. For example, a fluorine-labeled organic compound can be detected directly by measuring the ¹⁹F resonance.

Detailed Description Text (41):

V.sub.water, V.sub.oil, and V.sub.gas, are the relative volumes of water, oil, and gas in the NMR measurement section of the flow line. HI is the hydrogen index (proton density relative to pure water). W is the polarization time of the measurement, which can be controlled either by the time between pulse sequences, or the flow rate.

Detailed Description Text (42):

Oils with API gravity greater than 20, and with no dissolved gas, have proton density equal to that of water [Vinegar et al, "Whole Core Analysis by ¹³C NMR", SPE Formation Evaluation 6, 183-189 (June 1991)]. Most oil mud filtrates also have hydrogen densities equal to that of water. Gas is always a formation fluid; it is never a part of mud filtrates. A reduced proton density indicates gas, which is anticorrelated with the presence of mud filtrate in the flow line.

Detailed Description Text (47):

Trace Element Content: NMR measurements can also help distinguish water base mud (WBM) filtrate from formation water. There will be little or no contrast in viscosity, diffusion coefficient, proton density, or molecular conformation. However, the trace element content can be considerably different. Water soluble paramagnetic ions (either natural or introduced) will have a strong relaxing effect, which can be used to monitor proportions of filtrate and connate water.

Detailed Description Text (57):

Electron spin resonance (ESR) is useful because of its great sensitivity to unpaired electron spins, even at very low spin density. Unpaired electrons are found in naturally occurring or artificially introduced magnetic transition metal ions such as iron, manganese, chromium, cobalt, vanadium and nickel. These last two are frequently found in crude oils. Chromium is found at high concentration in a number of water base mud filtrates. Natural ground water has significant iron content. In general, mud filtrates and formation fluids will have different concentrations of transition metal ions, so ESR can be used to monitor the relative concentrations of filtrate and native fluids.

Detailed Description Text (58):

Unpaired electrons are also present in the free radicals of certain hydrocarbons, tertiary alkanes and alkyl benzenes, for example [Morrison and Boyd, Organic Chemistry, Allyn and Bacon, 1973]. The density of free radicals can be increased artificially by irradiating hydrocarbons with a low-level radioactive source located in the flow line upstream of the ESR cell. This can provide contrast between OBM filtrates and formation oils, which are likely to have differing amounts of compounds in which free radicals are stable.

Detailed Description Text (74):

V.sub.water, V.sub.oil and V.sub.gas are proportional to the volumes of each fluid. HI (hydrogen index) is the proton density for each fluid, normalized to the proton density of water at 20.degree. C. and 1 atmosphere pressure. The last factor on each line is a correction to account for insufficient polarization time W.

Detailed Description Text (77):

Oil: For oil at room temperature and pressure, without dissolved gas, hydrogen index is unity for API gravity greater than 20 [H. J. Vinegar et al, "Whole Core Analysis by 13C NMR", SPE Formation Evaluation, 6, 183-189 (1991)], which is the range of interest for fluid sampling tools. HI.sub.oil will track density as a function of temperature and pressure. There is no generally accepted correlation between HI.sub.oil and dissolved gas content.

Detailed Description Text (115):

Thus total salinity (maximum of [Na.sup.+] and [Cl.sup.-]) and an estimate of ion identity can be obtained, and used to estimate hydrogen index (see above), and water conductivity. The salinity is also important in estimating parameters for determination of density by gamma ray scattering or X-ray scattering.

CLAIMS:

8. The method of claim 7, wherein the indication of the contaminant comprises one of the following: viscosity, relaxation time, composition, trace element content, diffusion coefficient, proton density, and molecular conformation.
9. The method of claim 7, wherein the contaminant comprises a drilling mud filtrate.